

CHAPTER 29

PRIMARY CHEMICAL CELLS

In a chemical cell the reactions within the cell convert chemical energy to electrical energy. In Chapter 5 it was stated that provided two different type of materials are used as electrodes in a suitable electrolyte, an e.m.f. will be produced between the electrodes. When a load is connected to the terminals of the electrodes, current will flow in the external section of the circuit. In the previous Chapter it was explained that electrolyte dissociates in solution and provides a path for electrolytic current in electrolytic cells. The reactions in a chemical cell, however, are completely different from those in an electrolytic cell. Just how the reactions vary will be discussed in this Chapter. The author acknowledges the assistance given in this Chapter by 'Duracell'.

29.1 THE ELECTROMOTIVE SERIES

When two electrodes of different materials are immersed in an electrolyte, one will assume a positive potential while the other will assume a negative potential. The negative electrode will always be the electrode which has the highest combining ability with oxygen. The series listing the order of the combining ability of certain elements with oxygen or a negative ion is shown in Table 29.1.

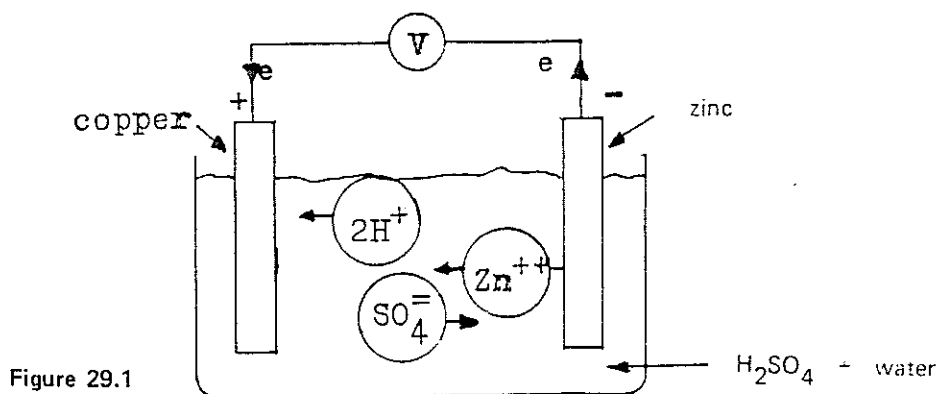
Table 29.1

1. Sodium
2. Zinc
3. Iron
4. Nickel
5. Lead
6. Hydrogen
7. Copper
8. Mercury
9. Silver
10. Gold

The elements at the top of the list more readily enter into combination than those elements listed below them. Thus zinc will be the negative terminal if teamed with copper while iron would be the negative terminal if used with nickel.

29.2 THE WET PRIMARY CELL

The combination of a zinc and a copper electrode in a solution of diluted sulphuric acid produces an e.m.f. of approximately 1.1 volts. This consists of 0.6 volts between the copper and the electrolyte and 0.5 volts between the zinc and the electrolyte. Different combinations of electrode material produce values of terminal e.m.f. that are dependant on their relative positions in the electromotive series. The chemical reactions at the anode and cathode of the zinc - copper cell are shown in Figure 29.1.



The zinc ions at the anode will readily combine with the sulphate ions in the electrolyte to produce zinc sulphate. In doing so, the zinc atoms will release two electrons which move through the external circuit to the copper cathode. At the cathode positive hydrogen ions accept the released electrons to form hydrogen gas. The hydrogen gas adheres to the cathode and gradually forms an insulating layer around the cathode. This insulating of the cathode is called polarisation. Polarisation results in a gradual decrease in e.m.f. produced at the terminals of the cell. The wet cell is rarely used commercially.

29.3 DRY CELLS

In dry cells the liquid electrolyte has been replaced with a paste electrolyte. There still has to be two different types of materials to produce an e.m.f. The materials are known as the anode and the cathode. The anode is the material by which current enters a cell. Chemical reactions occur within the cell that make the recharging of the cell impossible. For this reason dry cells are known as non-rechargeable cells. Initially there was only one dry cell, namely the zinc carbon cell, but modern technology has evolved many more types, some of which will be discussed in this Chapter.

29.4 CELL CONSTRUCTION

A cell consists of positive and negative current collectors, an anode, a cathode and an electrolyte. In some cells the current collectors may be the anode or cathode or both, but are always highly conductive materials. Zinc is the most widely used anode metal, not only because of its electrical properties but also because it is relatively inexpensive, easy to fabricate in various shapes, structurally strong and chemically stable. There are several other important anode metals, notably cadmium and lithium. Manganese dioxide (MnO_2) is the most common cathode material because it readily yields its oxygen, though other metallic oxides are used for special-purpose cells.

The electrolytes are a moist paste with one and sometimes several different substances. These substances may make the electrolyte solution either somewhat acid, or, conversely, they may make it alkaline. Either way, the nature of the actual mixture determines the electrical conductivity of the electrolyte.

For a variety of reasons relating to ease of manufacture and cell efficiency, most of the cells involved in the consumer business are cylindrical in design. A cylindrical shape is chemically efficient as well as, allowing one reactive material to be wrapped completely around another for maximum exposure between the two. The value of this will become clearer when looking at the actual design of some of the most important power cells.

The two major cell types involved in the consumer market are the traditional zinc carbon cell and the new, more durable and longer-lasting, alkaline manganese cell. And here there is some simple confusion in terminology which has grown up over the years that requires clarification. In the zinc carbon cell the anode is zinc, the electrolyte is mildly acid and the cathode is manganese dioxide. Imbedded in the cathode material is a carbon rod which serves as its current collector. Hence: zinc carbon. In the alkaline manganese cell, the anode is also zinc, the cathode is also manganese dioxide, but here the electrolyte is alkaline. Hence: alkaline manganese. Obviously there was no consistency in the naming of the two cell types. Still other cell types are named for the cathode material alone. Silver and mercury cells both have zinc anodes, but their cathodes are silver oxide and mercuric oxide respectively.

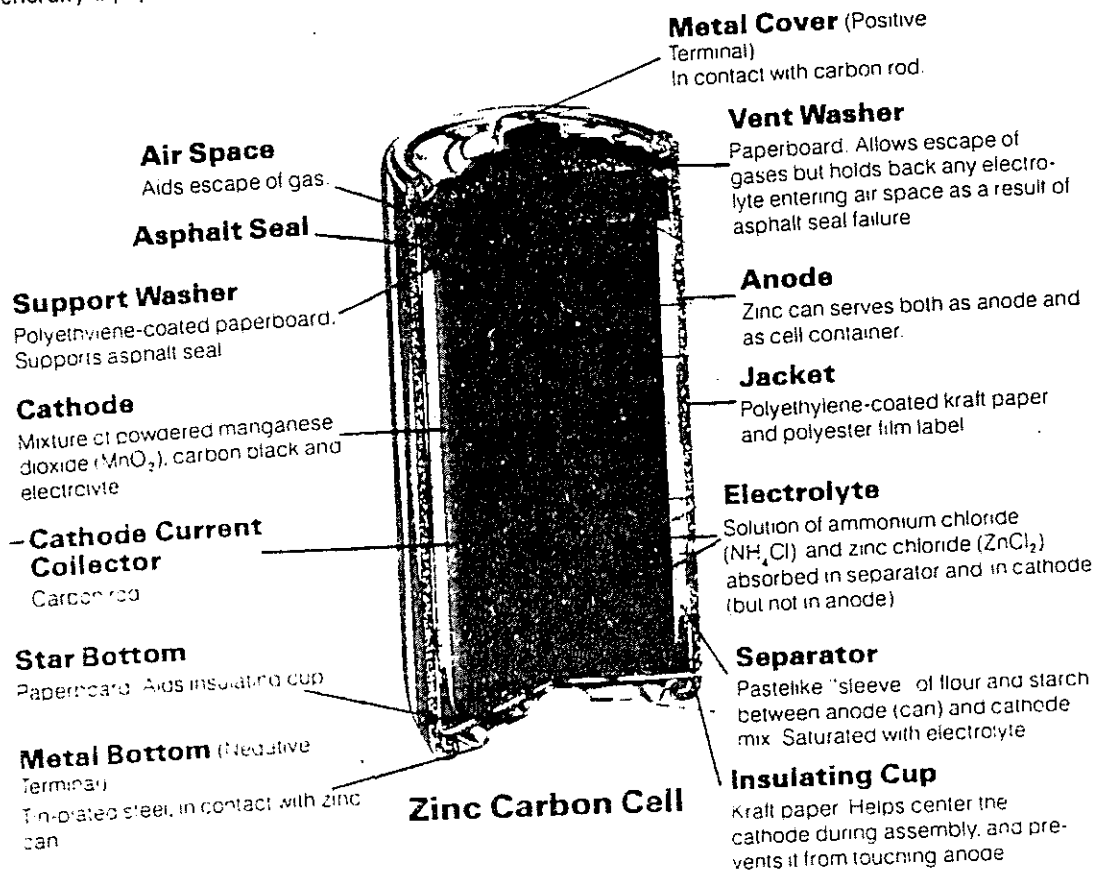
29.5 ZINC-CARBON CELLS

In the classic zinc carbon cell, the can that encloses the cell materials is made of zinc metal and functions as the anode as well. Such cans are easily extruded from zinc metal pellets. Lining the inside of the can is a paste-like sleeve made of flour and starch, saturated with electrolyte. This acts as a separator between the zinc anode can and the cathode, preventing the electrode materials from coming in direct contact and discharging spontaneously, or 'shorting out'. The paste-like sleeve also contains mercury in the form of mercuric chloride, which reacts spontaneously when the cell is first assembled, to lightly amalgamate the inner surface of the zinc can.

Within the sleeve is the cathode, a core of manganese dioxide (MnO_2) which is also infused with electrolyte to ensure adequate electrolyte contact to the interior. The electrolyte used in the zinc carbon cell is a solution of ammonium chloride (NH_4Cl) and zinc chloride (ZnCl_2), which is somewhat acidic (therefore corrosive).

Inserted into the manganese dioxide core is a carbon rod, which accounts for the other half of the 'zinc carbon' product description. It is in direct contact with the cathode material and acts as the current collector for the cathode. The anode current collector is formed at the bottom of the cell by pressing a metal end closure to the bottom of the zinc can.

Since inexpensive materials are a primary objective in the zinc carbon cell, the outer jacket is generally a paperboard construction. The general construction of a zinc carbon cell is shown in figure 29.2.



The zinc can which encloses the cell materials also functions as the anode. With the zinc doing double duty in this system, the cost of the cells is correspondingly reduced. There is a major disadvantage, however. If the zinc fails to oxidize uniformly during discharge and corrosion becomes excessive at certain spots, pin-hole perforations may occur in the can. Then, the somewhat acidic electrolyte will leak out, corroding other materials outside the cell.

The combination of the zinc electrode with the negative chloride ion in the electrolyte causes the zinc container to be consumed by the electrolyte, thus limiting the life of the cell. The reactions at the anode are irreversible, allowing the discharging of the cell to occur only once. For this reason the primary cell is said to be non-rechargeable. The zinc-carbon cell produces an open circuit t.p.d. of 1.5V.

The heavy duty zinc carbon cell is an improved version of the ordinary zinc carbon cell. While it is very similar in construction, it has a greater 'high drain' performance, meaning that it can deliver high currents for a longer period of time than the ordinary zinc carbon cell.

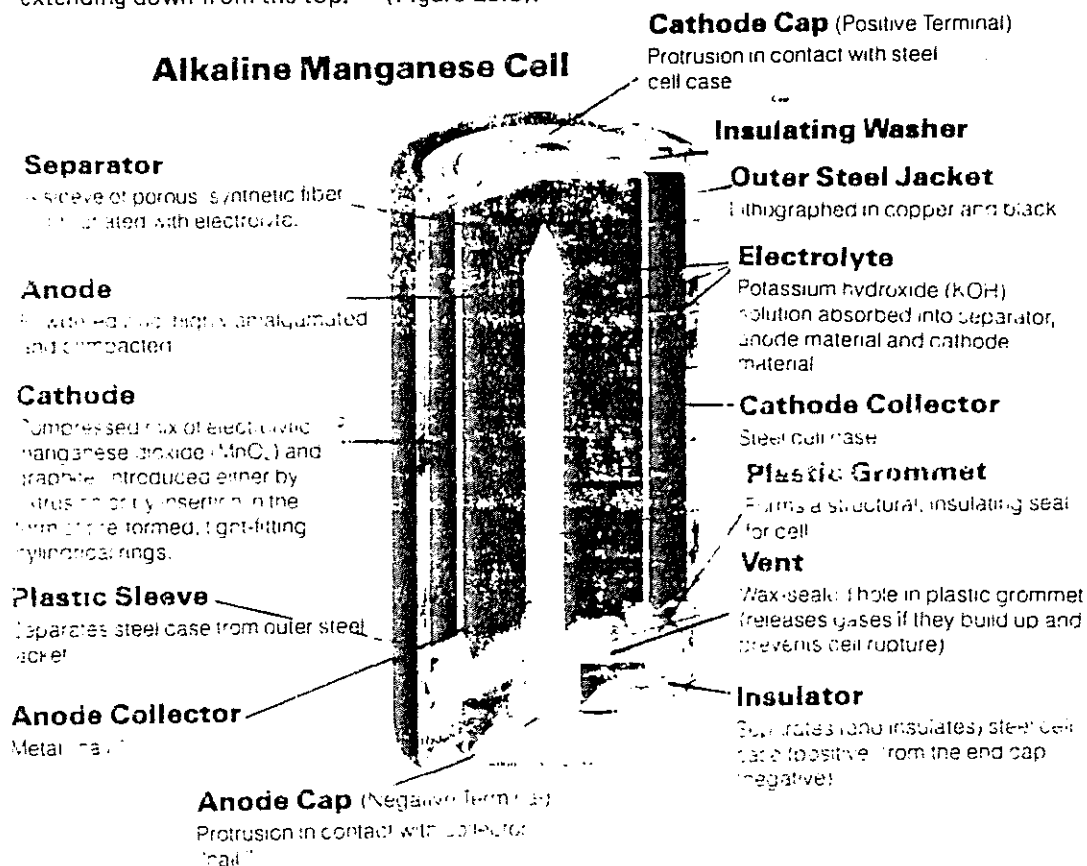
The major difference in most heavy duty cells is that the electrolyte is zinc chloride only, which has better performance characteristics. The use of zinc chloride has an added advantage as well: during discharge the cell becomes progressively drier. This reduces the likelihood of leakage if the cell is overloaded or drained excessively. High drain performance is also improved over the ordinary zinc carbon cell by the use of a higher quality blend of manganese dioxide in the cathode.

29.6 ALKALINE MANGANESE CELLS

To achieve performance which is far superior to ordinary zinc carbon cells in most applications, alkaline manganese cells require higher quality and more expensive materials, and a more sophisticated construction. Here the anode, which does not have to double as part of the cell structure, is formed of zinc powder. The zinc particles are of carefully controlled size, shape and purity, and are amalgamated (i.e. combined with mercury) to suppress gassing and to maximize performance at all discharge rates.

The alkaline electrolyte which gives this cell its popular designation is a solution of potassium hydroxide (KOH), which is highly conductive. The electrolyte is diffused throughout the powdered zinc and in intimate contact with all its tiny granules, insuring that the anode material is almost completely oxidized by the time the cell's stored energy is exhausted.

Similar design and engineering refinements apply to the cathode of the alkaline manganese cell. The basic cathode material is what is known as electrolytic manganese dioxide. This material is produced synthetically through electrolysis. Because the alkaline manganese cell has the same types of anode and cathode materials it produces the same e.m.f., namely 1.5V. In structural design the typical alkaline manganese cell is in many ways the exact opposite of the zinc carbon configuration. Here the anode is on the inside and the cathode is on the outside, instead of the other way around. And the alkaline cell has a central, nail-like anode collector inserted from the bottom, instead of a carbon-rod cathode collector extending down from the top. (Figure 29.3).



In the alkaline manganese system, the entire cell is enclosed in a steel case, which provides a considerably stronger and more secure container than the zinc can of zinc carbon cells. Just inside the steel case, and in intimate contact with it, is the cathode material. With this arrangement the can becomes the current collector for the cathode, with its positive terminal formed by a protrusion at the top of the case. Lining the thick, cylindrical cathode is a sleeve of absorbent material, which acts as a separator between cathode and anode, as in the zinc carbon cell. Within the sleeve is the zinc anode. Anode, cathode and separator are all infused with electrolyte for maximum capacity and conductivity, as has been suggested earlier.

At the core of the cell, in direct contact with the anode, is the so-called 'nail'. This forms the current collector for the anode and is welded to a cap at the bottom of the can to form the negative terminal of the cell. Because of this somewhat 'reverse' arrangement of design in the alkaline cell, the top terminal is positive just as it is in the zinc carbon cell (because of the carbon rod), and the bottom terminal is negative (provided by the bottom of the can in the zinc carbon system).

The development of the alkaline cell represented a tremendous breakthrough in primary power cell technology. For decades the industry remained locked into the zinc carbon system which, though it has been improved, was something of a dead end except for cheapness of manufacturing. But the alkaline system introduced new concepts of cell design. By employing higher grade, more compacted and energy-rich materials in anode and cathode, by using 'hotter' electrolytes and diffusing them throughout the reactive materials, and by enclosing the whole system in a sturdy steel case, it demonstrated that a far greater amount of energy could be stored with any standard cell size than had heretofore been thought possible. The result — along with improved shelf life, high drain performance and other attractive characteristics — has been a truly revolutionary power cell. The breakthrough also revealed that still greater horizons lie ahead for packaged power, with new shapes of things to come.

29.7 MAJOR DIFFERENCES BETWEEN ALKALINE MANGANESE AND ZINC CARBON CELLS

Both use a zinc anode and a manganese dioxide cathode, hence their voltages are nearly identical; however, the major differences between these cells are:

- (1) The zinc carbon cell uses one of the active ingredients as a structural component, that is, the zinc anode serves also as the can (or container) that encloses the cell materials.
- (2) The active materials in the alkaline manganese cell, since they are not used as structural components, can be optimized for their electrochemical function without regard to structural characteristics, and they can be heavily amalgamated for improved performance.
- (3) Because the zinc metal in the zinc carbon cell is in a compact form (in contrast to the powdered form in the alkaline manganese cell), it can only be penetrated by an acidic (not an alkaline) electrolyte, in cells where the quantity of electrolyte is limited.
- (4) The alkaline electrolyte in the alkaline manganese cell is a better ionic conductor than the acidic electrolyte in the zinc carbon cell.
- (5) The steel can (or case), which is an additional cost in the construction of the alkaline manganese cell, also provides a better and safer container for the system than the zinc can that encloses the zinc carbon cell materials.

29.8 BUTTON CELLS

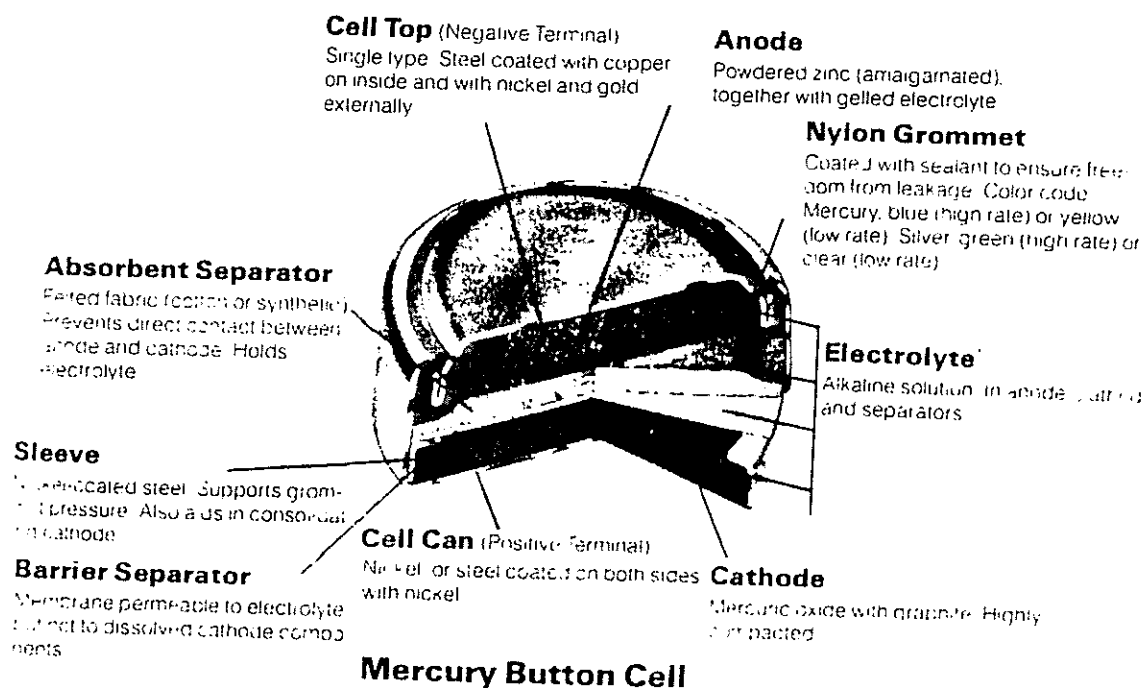
Another major cell design of considerable importance in the current consumer market is the 'button cell', so called because of the obvious button shape. The design meets a growing demand for cells with a sustained and reliable power output but of minimum size and weight — for such applications as hearing aids and digital watches, photographic equipment and heart pacemakers.

Generally button cells, because of their miniature size, require materials of the highest energy density if they are to have a reasonable capacity. Here, mercuric oxide, though expensive, offers many advantages as a cathode material because of its high oxygen content. Another widely used cathode material is silver oxide, which is also rich in oxygen and provides a higher voltage as well. In recent years a variant of this called 'divalent' silver oxide has found a limited market in some applications.

Because of the cost of materials, silver cells are even more expensive than mercury cells, without significant performance advantages in most major applications. There is one difference, however, that can be critical in some instances. Mercury systems characteristically produce a potential of 1.35 volts, by contrast to the 1.5 volt yield of zinc carbon and alkaline manganese cells. Silver oxide cells, however, provide a nominal 1.6 volts. In the past, certain transistor circuits, in some hearing aid and watch designs, have required the extra voltage and hence the silver cells to power them.

Because of the higher cost of silver and mercury, a number of button cells for the photographic maker have been designed around the alkaline manganese system. These cells are of necessity generally larger to make up for reduced capacity and obviously are used only when the space/performance requirements permit.

When it comes to construction, most types of button cells are formed similarly — and the process is quite simple. Both anode and cathode are pre-formed as pellets. They are then enclosed in a short cylindrical can, with appropriate barriers, insulators and seals, and the can is capped. The top of the can, in direct contact with the anode material, acts as its current collector. The bottom of the can plays a corresponding role for the cathode. (Figure 29.4).



While all button cells tend to look very much alike from the outside and are basically of similar design on the inside, the materials chosen are varied considerably to create the different performance characteristics required in such vastly different usages as watch batteries and hearing aids.

29.9 CELL UTILIZATION

In the general discussion of cells, the approximate open circuit e.m.f. of different types of cells was stated. This value of e.m.f. is the maximum value that can be produced by the cell, and rarely exceeds two volts. A single cell whose open circuit terminal potential difference (t.p.d.) is two volts would be useless if twelve volts is required to operate a device. The current that is drawn from a cell is not related to the materials of the electrodes, but to the surface area of the electrodes. An increase in electrode surface area increases the current that can be drawn from the cell. To produce voltages and current greater than those that can be obtained from a single cell, cells must be connected in series, parallel or series parallel.

29.10 SINGLE CELL CALCULATIONS

A cell may be regarded as an internal resistance connected in series with a source of zero resistance. (Figure 29.3).



This method allows the application of Ohm's Law to all problems involving the grouping of cells. Connecting the cell shown in Figure 30.1 to an external resistance (R_L) shows that the current drawn from the cells passes through the external resistance plus the internal resistance of the cell. (Figure 29.4).

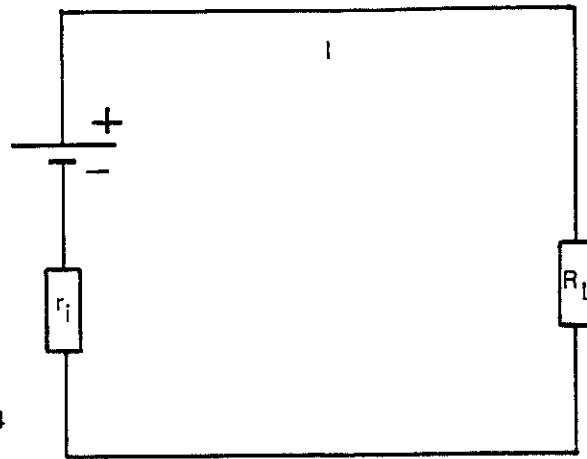


Figure 29.4

The total resistance (R) of the circuit is given by —

$$R = R_L + r_i$$

The current drawn from the cell is determined by applying Ohm's Law.

$$\begin{aligned} I &= \frac{E}{R} \\ &= \frac{E}{R_L + r_i} \end{aligned}$$

From Kirchhoff's voltage law, the sum of the voltages around a circuit is zero.

$$E - I r_i - I R_L = 0$$

$$E = I r_i + I R_L$$

This implies that a voltage drop exists within a cell whenever current is being drawn from the cell. The voltage E is regarded as a constant voltage source in the equivalent cell circuit, therefore the voltage drop across the load V_L must be $V_L = E - I r_i$.

Example 29.1

A cell has an open circuit e.m.f. of 1.5 volts and an internal resistance of 0.1 ohms. If the cell is connected to a load resistor of 2.9 ohms, calculate —

- Current drawn from the cell.
- Voltage drop across the load resistor.

$$\begin{aligned}
 E &= 1.5 \text{ V} \\
 r_i &= 0.1 \text{ ohms} \\
 R_L &= 2.9 \text{ ohms} \\
 I &= ? \text{ A} \\
 V_L &= ? \text{ V}
 \end{aligned}$$

$$\begin{aligned}
 R &= R + r_i \\
 &= 2.9 + 0.1 \\
 &= 3 \text{ ohms} \\
 I &= \frac{E}{R} \\
 &= \frac{1.5}{3} \\
 &= 0.5 \text{ A} \\
 V_L &= I R_L \\
 &= 0.5 \times 2.9 \\
 &= 1.45 \text{ V}
 \end{aligned}$$

Equations in this chapter

$$I = \frac{E}{r_i + R_L}$$

TUTORIALS 1.29

- (1) A dry cell has an internal resistance of 0.5Ω and an open circuit t.p.d. of 1.5 volts. Calculate the t.p.d. of the cell when it is supplying a 2.5Ω resistor.
- (2) A current of 0.2A is drawn from a cell having an open circuit t.p.d. of 1.5 volts and an internal resistance of 0.3Ω . Calculate the load t.p.d..
- (3) When a 2.9Ω resistor was connected to a cell whose open circuit t.p.d. was 1.5 V a current of 0.5A was drawn from the cell. Calculate the internal resistance of the cell.
- (4) Calculate the resistance of a load that would draw 0.75 A from a 1.5 V source whose internal resistance is 0.2 ohms.
- (5) When a resistor of 4.6Ω is connected to the terminals of a source whose internal resistance is 0.4Ω a current of 0.3 A flows through the resistor. Calculate the open circuit t.p.d. of the source.